

PATENT SPECIFICATION

(11) 1412486

- 1412486 (21) Application No. 7525/73 (22) Filed 15 Feb. 1973
 (31) Convention Application No. 175772 (32) Filed 15 Feb. 1972
 (31) Convention Application No. 175872 (32) Filed 15 Feb. 1972 in
 (33) Sweden (SW)
 (44) Complete Specification published 5 Nov. 1975
 (51) INT CL² C22B 7/00 C04B 5/00 7/00 7/08 7/14
 (52) Index at acceptance

C7D 20
 C1H 212 260 262 272 610 620 621 670
 C1K X



(54) RECOVERY OF METALLURGICAL SLAGS

(71) We, GRÄNGES AKTIEBOLAG, a Swedish Company, of 18, Gustav Adolfs torg, Stockholm, Sweden, do hereby declare the invention, for which we pray that a patent 5 may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:

This invention relates to a method of recovering metallurgical slags, particularly those containing more or less finely distributed metal and/or relatively high contents of metal oxides, for example slags from steel production, which satisfies the requirements of environmental protection and economy.

In melting and refining processes substantial quantities of slags are produced. Intensive efforts have been invested and many proposals have been made to utilize such 10 metallurgical slags. Interest has been focused on blast-furnace slags, about which an ample literature is now available, see for example Keil T.F. "Die Hochofenschlacke" (Blast-furnace slag) 2nd edition, Düsseldorf 1963.

The use of blast-furnace slags has become important from an economic point of view especially for the production of cement, but this covers only a minor part of the slag obtained.

Slags of a basic nature are obtained in very large quantities especially from steel production. Certain special slags of this type can be used as fertilizers, but for most of the slags there is no method of complete and economic recovery with utilization of the heat of the molten slag. In many cases the aforementioned types of slags include valuable metals, as for example Fe, Cr, Ni, and Mn, but yet they are dumped in slag yards. The slag content of oxides and more or less finely distributed metal is thereby lost. The latter, it is true, is sometimes recovered to some extent. In conventional slag handling a considerable loss is made by not utilizing the large amounts of heat included in the molten slag, to which loss are to be added the costs for handling the slag and for the

ground required for storage, for example for a slag dump. Dumping of slag, besides, is highly unsatisfactory from an environmental point of view.

The proposals which have been made, as mentioned above, for the treatment of blast-furnace slags in order to use them in the production of cement, refer in several cases to the addition of above all lime (CaO) to the melt in order either to obtain a slag which in the granulated and finely ground state is particularly suitable for mixing with portland cement, or to achieve directly a portland cement composition. It was found that this production of portland cement was technically feasible but not economic, i.e. because of the high temperatures required.

Some proposals for the treatment of blast-furnace slags suggest the use of containers lined with carbon bricks, because carbon bricks are resistant to reducing slags. Another reason was the desire to use an electrically conductive lining material.

It is also known that in several metallurgical processes the slag composition can be so controlled that the slag subsequent to grinding is directly adapted for use as aluminate cement. It is, however, a decisively restrictive factor for these processes that they require a slag with a high Al₂O₃ content, which, in the furnace, is in equilibrium with the metal being the main object to be achieved by the process.

In the British patent specification 1,229,955 a method for the production of hydraulic cement is proposed, in which reducing gases, preferably carbon monoxide or hydrogen gas, are used (not solid reducing agents), while heat is supplied by an oxidation process. It is apparent that the oxidation process disturbs the reduction process. Also, the desired reduction of manganese from manganese oxide with help of carbon monoxide and/or hydrogen gas at the temperatures indicated can take place only to a small extent.

Finally, one may say that all methods heretofore suggested are not applicable generally

50

55

60

65

70

75

80

85

90

2
and do not result in a complete economic recovery of slag.

The present invention provides a method of recovering a metallurgical slag containing metal oxide and, possibly, elementary metal, in which the molten slag is tapped into a container, carbon and material containing silicon or aluminium are added to reduce the metal oxide, the melt being maintained at a temperature preventing foaming while allowing sedimentation of the reduced metal and any elementary metal originally present, and the sediment and melt are separated, lime or aluminium-oxide-containing material being added to the melt in a quantity such as to give it the composition of an oxide mixture suitable for use in Portland cement or aluminate cement.

It is obvious to the expert that a contamination of the residue by, for example, oxides of Fe, Mn and similar colouring metal oxides would prevent the utilization of the residue as an additive to, for example, white cement. A considerable economic advantage is obtained by using as the aluminium containing material, bauxite heavily contaminated with iron oxide; a high-quality aluminate cement results, the iron having separated out during sedimentation.

For carrying out the method, a plant is required which in principle should comprise a reactor vessel, for example the ladle into which the slag is to be tapped, or a stationary container to which the slag or slags are to be transported for treatment, and which comprises a suitable equipment for the supply of heat, when required, which heat may be produced either electrically or by combustion. The plant further includes means for the addition of reducing agents and other additives to the slag. Pre-heating of the additives, which is important for the economy of the method, is ensured either by utilizing available combustible waste gas or by other heat generating installations known *per se*. The bottom portion of the reactor vessel advantageously is provided with a suitable tapping device for the removal of sedimented metals originating from the process in which

the slag was formed and from the reduction of the slag according to the method of the invention. The plant will also include installations in which the residue (removed slag) is caused to solidify at the speeds desired for obtaining a suitable structure and form of the products.

As regards the chemical composition of the metallurgical slags treated according to the invention, the SiO₂-content normally is above 10%.

It is again emphasized that the control of the viscosity during the reduction process is of the highest importance. When, for example, heat is added by the combustion of, e.g., carbon or oil with oxygen, prior to reduction with carbon, the difficulty may arise that the temperature, which ensures the desired fluidity, cannot be held continuously, because the reduction process with carbon consumes heat. The resulting lowering of the temperature brings about foaming. In such a case one operates intermittently, i.e., by the steps of supplying heat, reducing, tapping metal, supplying heat again, and so on, until the residue has the desired composition.

It has been found that the method according to the invention is advantageous for processing or regenerating (refining) waste products which contain metallic substances in the elementary state or in the form of chemical compounds, such as grindings, waste products, from the chemical industry, heavily contaminated metals scale, neutralization products, dross, etc. These waste products are added to the slag prior to reduction.

The method according to the invention is of general applicability, and its complete exemplification would be unusually extensive. In the following, therefore, only some examples are given to illustrate the main features of the invention.

In the Examples, % refers to % by weight.

Example 1.

In a lined ladle, 20 tons of a basic steel-making slag were tapped, having a temperature of 1600°C and the following composition:

| CaO | SiO ₂ | Al ₂ O ₃ | AgO | FeO | MnO | P ₂ O ₅ |
|-----|------------------|--------------------------------|------|-----|-----|-------------------------------|
| 50% | 16% | 1.7% | 2.5% | 15% | 6% | 1.5% |

100 In addition, the slag contained 10% of metallic iron. The ladle was placed under an arc furnace roof, and the slag was reduced by the addition of fine-grained petroleum coke and the supply of electrical energy. In order to avoid excessive expansion of the slag it was necessary to heat the slag to a temperature at which it was sufficiently fluid. At the same time bauxite (71% Al₂O₃, 4% SiO₂, 23% FeO) preheated to 1000°C was added. The bauxite was preheated in a shaft

placed above the furnace roof, where the waste gases from the reduction were burned. The reduction was completed with an addition of aluminium metal.

The total additions during a treatment time of 70 minutes were 1.3 tons of coke, 10.1 tons of preheated bauxite, and 1.2 tons of aluminium, 4.4 MWh of electrical energy were supplied.

On tapping 8.1 tons of metal (spiegeleisen) were obtained, having a composition of 12%.

95

90

85

80

75

70

65

60

55

50

Mn, 11% Si, and 1.6% P. Furthermore, a residue of 23 tons was left, having the following composition:

| | CaO | SiO ₂ | Al ₂ O ₃ | MgO | S |
|---|-------|------------------|--------------------------------|------|------|
| 5 | 44.6% | 7.6% | 45.0% | 2.2% | 0.1% |

The residue was teemed into moulds,

| | CaO | SiO ₂ | Al ₂ O ₃ | MgO | FeO | MnO | P ₂ O ₅ |
|----|-----|------------------|--------------------------------|------|-----|-----|-------------------------------|
| 15 | 49% | 16% | 1.5% | 6.5% | 15% | 6% | 1.5% |

was reduced with carbon.

During the reduction bauxite (60% Al₂O₃, 17% SiO₂, 20% FeO) preheated to 1000°C was added (as the aluminium-containing material) and furthermore SiO₂ in the form of sand (as the silicon-containing material).

There was added, per ton of treated slag: 280 kg preheated bauxite and 63 kg sand,

| CaO | SiO ₂ | Al ₂ O ₃ | MgO | FeO | MnO | S | Alkali |
|-------|------------------|--------------------------------|------|------|------|-------|--------|
| 44.2% | 27.5% | 16.2% | 7.4% | 0.4% | 0.7% | 0.10% | 0.19% |

35 The granulate after grinding to the fineness of cement showed excellent hydraulic properties. Thus, with activation of only 20% portland cement and with 4% gypsum added, values of compressive strength after 3, 7, and 28 days were measured which were at maximum only 8% less than the corresponding values for pure portland cement.

Example 3.

In a modification of the process according to Example 2, the slag temperature was increased towards the end of the reduction process to over 1600°C, and the reduction completed by introduction of aluminium metal. The resulting granulated slag then contained

| CaO | SiO | Al ₂ O ₃ | MgO | S | Alkali |
|-------|-----|--------------------------------|-----|------|--------|
| 44.2% | 38% | 10% | 6% | 1.3% | 1.5% |

65 The reduction was performed according to Example 2 with the exception that no sand was added.

The residue had the following composition:

| CaO | SiO ₂ | Al ₂ O ₃ | MgO | S | Alkali |
|-------|------------------|--------------------------------|------|------|--------|
| 44.1% | 30% | 13.1% | 6.7% | 0.7% | 0.8% |

70 WHAT WE CLAIM IS:—

1. A method of recovering a metallurgical slag containing metal oxide and, possibly, elementary metal, in which the molten slag is tapped into a container, carbon and material containing silicon or aluminium are added to reduce the metal oxide, the metal being maintained at a temperature preventing foaming while allowing sedimentation of the reduced metal and any elementary metal originally present, and the sediment and melt are separated, lime or aluminium-oxide-contain-

ing material being added to the melt in a quantity such as to give it the composition of an oxide mixture suitable for use in Portland cement or aluminate cement.

85

2. A method as claimed in claim 1, in which lime is added to the melt to give it a composition suitable for use in Portland cement, the material containing silicon or aluminium comprising elementary silicon or aluminium.

25

3. A method as claimed in claim 1 or 2, in which, before reduction of the slag, one

30

and 4.9 kg carbon; 203 kWh of electrical energy were supplied. There was obtained per ton of slag 290 kg spiegelisen with 14% Mn, 2% Si, and 1.3% P, and 1040 kg of residue.

The residue was granulated with water from a slag temperature of 1560°C and had the following composition:

50

only 0.1% FeO and 0.1% MnO and was completely white.

On activating the ground granulate with 20% of conventional white cement, a cement was obtained which remained white also under hydration and did not show the blue-black colouring that normally occurs under hydration of cements containing blast furnace cement.

55

Example 4.

A basic steelmaking slag according to Example 2 was tapped into a stationary furnace together with the same quantity of blast furnace slag, having the following composition.

60

| CaO | SiO | Al ₂ O ₃ | MgO | S | Alkali |
|-------|-----|--------------------------------|-----|------|--------|
| 44.2% | 38% | 10% | 6% | 1.3% | 1.5% |

ing material being added to the melt in a quantity such as to give it the composition of an oxide mixture suitable for use in Portland cement or aluminate cement.

85

2. A method as claimed in claim 1, in which lime is added to the melt to give it a composition suitable for use in Portland cement, the material containing silicon or aluminium comprising elementary silicon or aluminium.

90

3. A method as claimed in claim 1 or 2, in which, before reduction of the slag, one

or more waste products containing elementary metal or metals or metallic compounds are supplied to the slag in the container.

4. A method of recovering a metallurgical

slag, substantially as described herein in any of the Examples given.

MARKS & CLERK.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.